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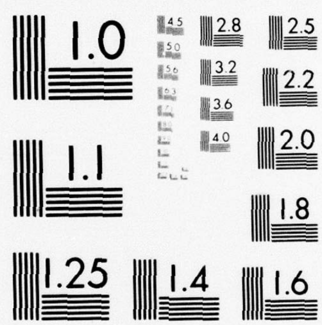

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The Structure and Magnetic and Electrical Conductivity Properties of the Charge Transfer Compound 1,1'-Dimethylferrocenium Bis(Tetracyanoquinodimethane), $[(CH_3C_5H_4)_2Fe][TCNQ]_2$.

by

(10)

Scott R. Wilson, Peter J. Corvan, Reginald P. Seiders, Derek J. Hodgson, Maurice Brookhart, William E. Hatfield, Joel S. Miller, Arthur H. Reis, Jr., P.K. Rogan, Elizabeth Gebert and Arthur J. Epstein

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The charge transfer compound 1,1'-dimethylferrocenium bis(tetracyanoquinodimethane) has been prepared and characterized by a single crystal x-ray structure determination, magnetic susceptibility studies, and conductivity measurements. The structure consists of chains of stacked TCNQ molecules and stacked ferrocenium ions, but there are no intermolecular interactions in the latter chains.

THE STRUCTURE AND MAGNETIC AND ELECTRICAL CONDUCTIVITY PROPERTIES OF THE CHARGE TRANSFER COMPOUND 1,1'-DIMETHYLFERROCENIUM BIS-(TETRACYANOQUINODIMETHANE), $[(CH_3C_5H_4)_2Fe][TCNQ]_2$.

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Metallocenes react with tetracyanoquinodimethane (TCNQ) to yield charge transfer compounds predominantly of the stoichiometry [metallocene][TCNQ] or $[\text{metallocene}][\text{TCNQ}]_2$.[1,2] The 1:2 compounds have relatively high electrical conductivities which range from 4 $ohm^{-1}cm^{-1}$ for $[(C_5H_5)_2Fe][TCNQ]_2$ to 0.03 $ohm^{-1}cm^{-1}$ for $[(CH_3C_5H_4)_2Fe]$-$[TCNQ]_2$,[1] but, up to now, difficulties in obtaining high quality single crystals have prevented structural determinations.

The recent report[3] of the use of Sephedax gels for the growth of single crystals led us to use this technique in the case of $[(CH_3C_5H_4)_2Fe][TCNQ]_2$.

Experimental Section:

The title charge-transfer complex was prepared by reaction of 1,1'-dimethylferrocene and TCNQ (molar ratio 1:2, respectively) in hot acetonitrile solution. Dark needles were isolated by filtration of the cooled solution. A portion of this material was dissolved in a minimum volume of hot acetonitrile and the resulting dark green solution was poured into a warm test tube (1.5 x 12 cm). Immediately, Sephadex LH-20 (Pharmacia Fine Chemicals) was added until all the acetonitrile had been absorbed. The test tube was allowed to cool slowly, and within 30 minutes small rectangular prisms of the complex began growing inside the gel. After one day at room temperature, the gel was then broken up with distilled water and individual crystals were removed for study.

For the preparation of dimethylferrocenium hexafluorophosphate, dimethylferrocene (4.0 mmole) was oxidized by stirring in dilute nitric acid for 2 hours at which time dissolution was nearly complete. The addition of ammonium hexafluorophosphate to the filtered solution produced a blue-grey precipitate of the PF_6^- salt. This material was then rapidly recrystallized from anhydrous methanol to give 0.22 g (15% yield) of the PF_6 salt as a green-grey powder, whose formulation was confirmed by elemental analysis.

Magnetic properties were measured using a PAR vibrating sample magnetometer. Temperatures were measured with a calibrated gallium/arsenide diode by observing the voltage on a Dana Model 4700 4.5 place digital voltmeter. Details of the experimental techniques have been given elsewhere.[4]

Crystallographic Section:

Two entirely separate sets of data were collected, one at Argonne National Laboratory and the other at the University of North Carolina; the following discussion pertains to the latter set, since these data were obtained from a crystal synthesized by the method described above. The two data sets are, however, of comparable quality, and the derived structural parameters are equal with standard deviations.

On the basis of precession and Weissenberg photography, the intensely dark blue prismatic crystals were assigned to the triclinic system, the space group being either $P\bar{1}$ or P1; the former choice was confirmed by the successful refinement of the structure. The cell constants, obtained by least-squares methods from the diffractometer settings of twelve reflections with $2\theta(\text{Mo}) \geq 25°$, are $\underline{a} = 7.660(2)$, $\underline{b} = 7.530(2)$, $\underline{c} = 14.083(4)$ Å, $\alpha = 83.83(2)°$, $\beta = 110.42(2)°$, $\gamma = 94.48(2)°$. The observations were made at 22°C with the wavelength assumed as $\lambda(\text{MoK}\alpha_1) = 0.70926$ A. A density of 1.35(1) g cm^{-3} observed by flotation in chloroform/dichloromethane solutions is in acceptable agreement with the value of 1.370 g cm^{-3} calculated for one formula unit per cell. Hence, in space group $P\bar{1}$ the iron atom is constrained to lie on a crystallographic inversion center.

Diffraction data were collected from a prismatic crystal bounded by the (001), (00$\bar{1}$), (100), ($\bar{1}$00), (0$\bar{1}$0), and (01$\bar{1}$) faces. The approximate crystal dimensions were 0.51 x 0.16 x 0.11 mm in the [100], [001], and [010] directions, respectively. The crystal was mounted approximately parallel to the crystallographic $\underline{a}$ axis, and intensity data were collected on a Picker four circle automatic diffractometer equipped with a molybdenum tube and a graphite monochromator. Data were collected by the $\theta/2\theta$ scan technique at a scan rate of 1.0°min.$^{-1}$. To allow for the presence of both Kα_1 and Kα_2 radiations, peaks were scanned from 1.0° in 2θ below the calculated Kα_1 peak position to 1.0° in 2θ above the calculated Kα_2 peak position. Stationary-counter, stationary-crystal backgrounds were counted for 20s at each end of the scans. A unique data set having 2θ(MoKα) $\leq$ 55° was gathered, a total of 3747 reflections being collected. The intensities of three standard reflections, examined after every 100 reflections, remained essentially constant throughout the run.

The data were processed by the method of Ibers and coworkers.[5] After correction for background, the intensities were assigned standard deviations as

$$\sigma(I) = [C + 0.25(ts/tb)^2(B_H + B_L) + (pI)^2]^{\frac{1}{2}}$$

where the symbols have their usual meanings[5] and the value of p was assigned as 0.04. The values of I and σ(I) were corrected for Lorentz-polarization effects[6] and for absorption.[7] The absorption coefficient μ for these atoms with MoKα radiation is 5.28 cm^{-1}, and for the sample chosen the transmission coefficients ranged from 0.92 to 0.96. Of the 3747 intensities recorded, only 1599 were independent data with I > 3σ(I); only these data were used in the structure analysis.

The structure was solved by direct methods using the highest 256 normalized structure amplitudes (E's) in the program MULTAN.[8] Because of some pseudo symmetry, the data with h = 2n had to be scaled separately from those with h = (2n + 1). The resulting E-map revealed the locations of the TCNQ carbon atoms and the iron atom (constrained to lie on an inversion center). Isotropic refinement of these positions led to values of the conventional agreement factors $R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$ and $R_2 = [\Sigma w(|Fo|-|Fc|)^2/\Sigma w(Fo)^2]^{\frac{1}{2}}$ of 0.281 and 0.364, respectively. All least-squares refinements were on F, the function minimized being $\Sigma w(|Fo|-|Fc|)^2$ with the weight w being assigned as $4Fo^2/\sigma^2(Fo^2)$. The scattering factors were taken from the usual sources.[9]

The carbon atoms of the methylcyclopentadienyl moiety were located in a difference Fourier map. Eventual anisotropic refinement of these atoms led to R_1 = 0.072, R_2 = 0.077. Addition of the four hydrogen atoms in the TCNQ moiety, refined isotropically, gave R_1 = 0.064, R_2 = 0.065. At this stage of refinement the C-C ring bond lengths in the methylcyclopentadienyl moiety were rather short, ranging from 1.33 to 1.39 Å, and the Uij's were very large; these observations could be attributable to some disorder, which is extremely common for systems of this type,[10] but attempts to refine a disordered model were unsuccessful. Addition of the remaining hydrogen atoms led to $R_1 = 0.059$; a difference Fourier at this stage was featureless with no peak higher than 0.5 eA^{-3}.

Description of the Structure:

The structure consists of $Fe(CH_3C_5H_4)_2$ and TCNQ units. The iron atom lies on a crystallographic inversion center. The TCNQ moieties also lie on inversion centers, there being two crystallographically independent "half-TCNQ" moieties. The packing of these fragments in the crystal is shown in Figures 1 and 2. As is seen in Figure 2, one TCNQ unit (A) approaches neighboring iron atoms (through its terminal CN groups) much more closely than does the

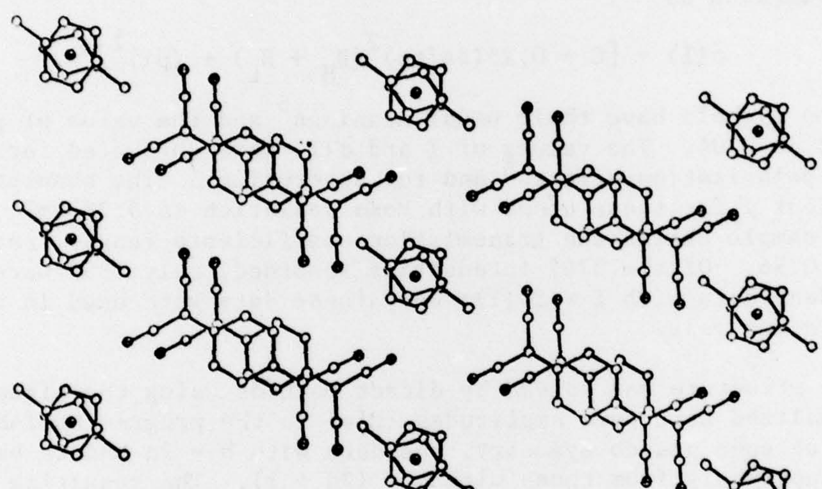

Figure 1. A view of structure of 1,1'-dimethylferrocenium $(TCNQ)_2$ along the a axis which shows the slipped nature of the TCNQ stacks.

other (B). As is seen in the figures, the structure can be viewed as consisting of chains of $CH_3C_5H_4$ (MeCp) rings separated by parallel chains of TCNQ units; the direction of the chains is the crystallographic a-axis. The MeCp and TCNQ rings are not normal to the chain direction, however; in the MeCp chain the angle between the normal to the planes and the a-axis is 9.1°, while in the TCNQ chain the average value is 14.2°.

In the MeCp chains, there are two distinct separations; the rings involved with any given Fe atom are separated by 3.41 Å

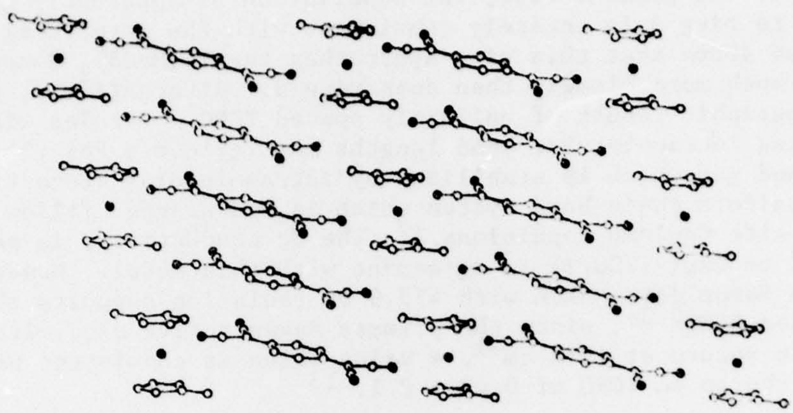

Figure 2. A view of the structure of 1,1'-dimethylferrocenium $(TCNQ)_2$ along the b axis which shows the parallel stacks of ferrocenium ions and TCNQ units.

while neighboring rings are separated by 3.63 Å. The units in the TCNQ chains are equally spaced, the center of each ring lying on an inversion center; the separation between each ring center is simply a/2 as measured along a. Since the rings are not normal to the chain direction, however, the interplanar separation is only 3.23 Å.

The two TCNQ units are crystallographically distinct and are much more precisely determined than the MeCp rings because of the high thermal motion (or disorder) of the latter. The rings each display the expected quinoidal geometry, with two "double" bonds and four "single" bonds. In the A ring these are of lengths 1.343(7) and 1.425(6) and 1.433(6) Å, respectively, while in the B ring the values are 1.334(7), 1.436(6), and 1.438(6) Å, respectively. The four terminal C-N bond lengths are all very similar, with values of 1.139(6), 1.139(6), 1.140(6), and 1.145(6) Å. There appears to be a significant difference, however, between the extracyclic nominally double C-C bonds in the two rings; in ring A this has the length 1.395(6) Å, while in ring B it is 1.378(6) Å. This small but significant difference, which is independently confirmed in the Argonne analysis, has been observed by other workers in related systems[11] and can be attributed to an increase in radical character on ring A relative to that on B. In neutral TCNQ this distance is 1.374 Å, in $TCNQ^-$ it is 1.418 Å and in the system reported as $TCNQ^{\frac{1}{2}-}$ it is 1.388 Å; hence, it is apparent that this C=C distance is extremely sensitive to electron donation from donors in the crystal.[11] In the present case, the observation of apparently greater donation to ring A is entirely consistent with the structural feature noted above that this ring approaches the $Fe(MeCp)_2$ donor moieties much more closely than does ring B. Alternatively, this crystallographic result of uniformly spaced TCNQ molecules with alternating intramolecular bond lengths may reflect a Peierls distortion and gap which is stabilized by intramolecular distortion in this uniform chain band system which is one-quarter filled with large on-site Coulomb repulsions.[12] The dc conductivity is proportional to exp(-1200/T) in agreement with this model. However, resonance Raman data taken with 457.9 nm radiation supports the formulation $TCNQ^{0.5-}$, since the primary Raman active exocyclic C-C absorption occurs at 1428 cm^{-1}, a value which is consistent with a negative charge on TCNQ of 0.42 ± 0.1.[13]

Magnetic Properties:

The temperature variation of the magnetic susceptibility of a powdered sample of $[(CH_3C_5H_4)_2Fe][TCNQ]_2$ was determined in the temperature range 4.2 to 76°K. The data are presented in Figure 3 as a plot of the reciprocal of the molar susceptibility versus temperature. The data may be fit very precisely by the Curie-Weiss Law

$$\chi = \frac{C}{T-\theta}$$

where $C = Ng^2\beta^2S(S+1)/3k$ with $g = 2.837$ and $\theta = -0.732°$. The best fit of the Curie-Weiss Law to the data is shown as the solid line in Figure 3. The average g value determined from the magnetic susceptibility data agrees nicely with an average g value of 2.79 which may be calculated from the EPR data for 1,1'-dimethylferrocenium hexafluorophosphate using the expression

$$g_{ave}^2 = 1/3(g_{||}^2 + 2g_{\perp}^2)$$

and the observed $g_{||} = 4.002$ and $g_{\perp} = 1.92$.[14] For the purpose of comparison, magnetic susceptibility data for 1,1'-dimethylferrocenium hexafluorophosphate are plotted as open squares in Figure 3. The close agreement of the data for the two compounds leads to the conclusion that the susceptibility in this temperature region is dominated by the 1,1'-dimethylferrocenium cation, and more remarkably, to the conclusion that these cations, although packed closely in the crystal structure, do not exhibit appreciable intermolecular spin-spin interactions.

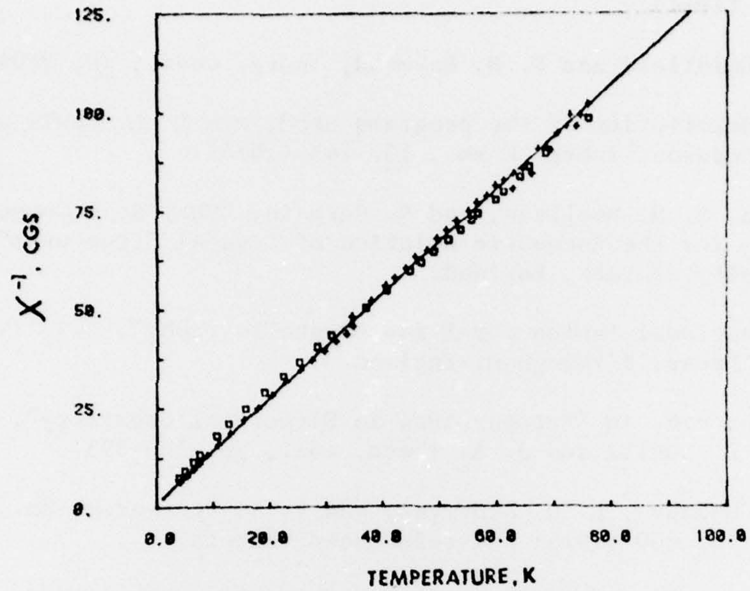

Figure 3. The inverse susceptibility of 1,1'-dimethylferrocenium $(TCNQ)_2$ (+) and 1,1'-dimethylferrocenium $(PF_6)_2$(□) as a function of temperature. The solid line is the best fit to the Curie-Weiss law for the TCNQ charge transfer compound.

Acknowledgement

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References

1. L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, J. Amer. Chem. Soc., 84, 3374 (1962).

2. J. S. Miller, A. H. Reiss, Jr., and G. A. Candela, Lecture Notes in Physics, in press.

3. G. R. Desiraju, D. Y. Curtin, and I. C. Paul, J. Amer. Chem. Soc., 99, 6148 (1977).

4. D. B. Losee and W. E. Hatfield, Phys. Rev. B, 10, 212 (1974).

5. P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, Inorg. Chem.,

6, 197 (1967).

6. S. A. Goldfield and K. N. Raymond, Inorg. Chem., 10, 2604 (1971).

7. For a description of the programs used, see D. L. Lewis and D. J. Hodgson, Inorg. Chem., 13, 143 (1974).

8. P. Main, M. M. Woolfson, and G. Germain, "MULTAN: A Computer Program for the Automatic Solution of Crystal Structures", University of York, England.

9. "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England.

10. F. Herbstein, in "Perspectives in Structural Chemistry", Vol. IV, J. D. Dunitz and J. A. Ibers, eds., pp. 166-395.

11. R. P. Shibaeva, L. O. Atovmyan, and V. I. Ponomarev, Zh. Str. Khim., 16, 860 (1975) and references therein.

12. E. M. Connell, A. J. Epstein, and M. J. Rice, Proc. Int. Conf. on Quasi-One-Dimensional Conductors, Dubrovnik, Yugoslavia, Sept. 4-8, 1978. (Springer-Verlay, to be published).

13. T. W. Cape and R. P. Van Dyne, private communication.

14. D. M. Duggan and D. N. Hendrickson, Inorg. Chem., 14, 955 (1975).

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